

XI. *On the Electrical Conductivity of Flames Containing Salt Vapours.*

By HAROLD A. WILSON, *B.Sc. (Lond. and Vic.), 1851 Exhibition Scholar,*  
*Cavendish Laboratory, Cambridge.*

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IN a recent paper\* on the electrical conductivity and luminosity of flames containing salt vapours, by Professor A. SMITHELLS, Mr. H. M. DAWSON, and the writer, the similarity between the conductivity of flames and that of gases exposed to Röntgen rays was pointed out, and it was shown that the relation of the current between two electrodes in the flame to the potential difference between them could be represented by the formulæ

$$I - i = k_2 \frac{i^2}{E^2},$$

$$C = i + k_1 E,$$

where  $C$  = the current,

$E$  = the P.D. between the electrodes.

$I$ ,  $k_1$ ,  $k_2$  are constants, and  $i$  is defined by the second equation.

When  $E$  is large, these equations become

$$C = I + k_1 E,$$

and if  $k_1 = 0$ , then they reduce to

$$I - C = k_2 \frac{C^2}{E^2},$$

which represents the relation between the current and P.D. for the conductivity of Röntgenised gases. (See a paper by J. J. THOMSON and E. RUTHERFORD, 'Phil. Mag.,' Nov., 1896.)

The experiments described in the present paper were undertaken with the object of following up the analogy between the conductivity of salt vapours and that of Röntgenised gases, and especially of getting some information about the velocities of the ions in the flame itself.

The paper is divided into the following sections :—

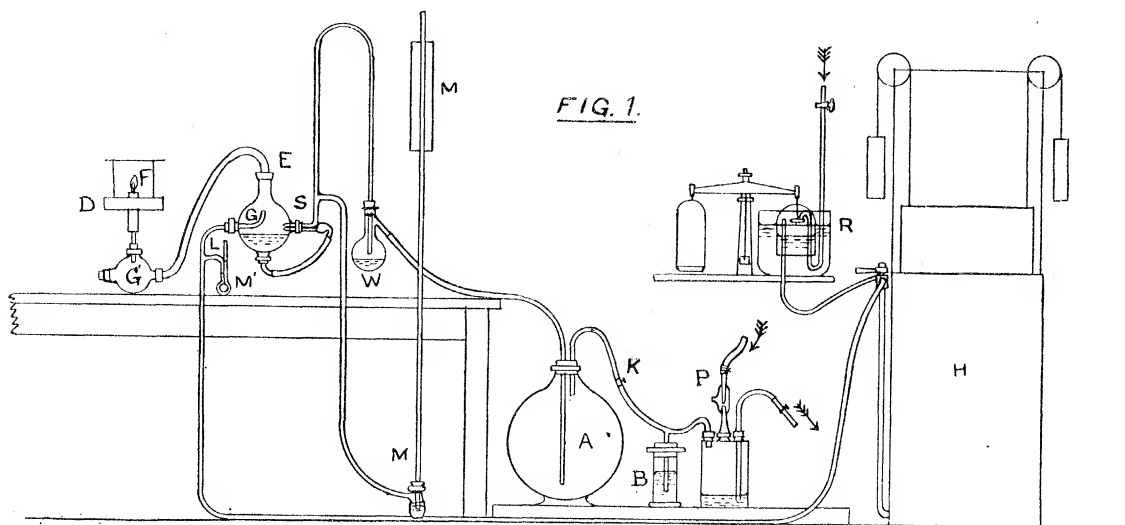
\* Abstract at 'Roy. Soc. Proc.,' vol. 64, p. 142.

- (1.) Description of the apparatus for producing the flame.
- (2.) The relation between the current and E.M.F. in the flame.
- (3.) The fall of potential between the electrodes.
- (4.) The ionisation of the salt vapour.
- (5.) The relative velocities of the ions in the flame.
- (6.) The relative velocities of the ions in hot air.
- (7.) Conclusion.

A summary of the earlier work done on this subject is given in WIEDEMANN'S 'Lehre von der Elektrizität,' vol. 4 B. ARRHENIUS'S paper ('Wied. Ann.,' vol. 42, 1891) is referred to in our paper mentioned above.

(1.) *Description of the Apparatus used for Producing the Flame.*

The apparatus used for producing the flame was similar in principle to that used in the investigation referred to above. Carefully regulated supplies of coal gas and air were mixed together, along with spray of salt solution, and the mixture burnt from a brass tube, 0.7 centim. in diameter. The apparatus is shown in fig. 1.



- |                      |                                    |                      |
|----------------------|------------------------------------|----------------------|
| P, Water pump.       | M M', Water manometers.            | E, Exit tube from G. |
| B, Mercury blow-off. | R, Gas regulator.                  | G', Second globe.    |
| A, Carboy.           | H, Gasometer.                      | F, Flame.            |
| W, Water flask.      | L, Constriction.                   | D, Wood block.       |
| S, Gouy sprayer.     | G, Globe containing salt solution. |                      |

The air supplied by the water pump, P, partly escapes by bubbling through mercury in B, and then passes into a carboy, A. From A the air passes through a flask, W, containing water, to the Gouy sprayer, S, and its pressure is measured by the water manometer, M. The air supply is regulated by means of a pinch-cock, K, and by

altering the water supply to the pump. A very considerable change in the water supply was necessary to appreciably alter the pressure indicated by the manometer, M. The air pressure used was 180 centims. of water, and it was very easily kept constant within 2 or 3 millims., only very occasional adjustments being required for this.

The coal gas was passed through a regulator, R, consisting of a bell-jar suspended in water from one arm of a balance and arranged as shown in fig. 1, so that, when the gas in the jar attained the required pressure, the jar rose and cut off the gas supply. After passing through this regulator the gas supply was connected with a gasometer, H, which served to maintain the pressure steady. The weights on the gasometer were adjusted so as to produce a pressure equal to that at which the regulator partly cut off the gas. The gas was passed through a constriction, L, and then allowed to mix with the air and spray from the sprayer, S, in the globe, G.

The pressure of the gas supply was measured on the water manometer, M', by means of a cathetometer reading easily to 0.01 centim. The gas pressure used was 3.62 centims. of water, and it was easily kept constant within 0.01 centim. by occasionally altering the weights on the gasometer and in the pan of the balance.

The mixture of gas and air passed along the tube, E, into a globe, G', and from this into the flame tube, T. The tube, T, was supported by a wider brass tube, provided at its upper end with three screws for centring the flame tube, and fixed into an octagonal wooden block, D, 3.5 centims. thick and 20 centims. across (see fig. 2). A cylindrical glass shade, 15 centims. in diameter and 16 centims. high, rested in a circular groove in the block, D, and on this a flat tin plate was placed, having a circular hole at its centre, 3 centims. in diameter, for the escape of the products of combustion. Three holes, each 1 centim. in diameter, in the block admitted air to the flame, F.

The flame thus obtained was steady, and measurements of its conductivity, when a particular salt solution was sprayed, did not differ more than 1 or 2 per cent. on different days.

The gas consumed by the flame amounted to 43 litres per hour. The height of the inner sharply-defined green cone was 1.5 centim., and that of the outer cone 7.5 centims.

## (2.) *The Relation between the Current and E.M.F.*

Some experiments were first done on the relation between the current and E.M.F. in the flame. The electrodes used each consisted of a brass disk, 14 centims. in diameter and 0.2 centim. thick, having a circular hole 5.6 centims. in diameter at its centre, covered with a grating of platinum wires (see fig. 2).

These two disks were each supported by three glass rods horizontally one above the other symmetrically about the axis of the flame. Two parallel slots were cut on each side of the hole in the upper disk, and through these the platinum gauze was

stretched across and kept in position by two brass strips screwed down over the slots. The gauze was thus stretched across the under side of the upper disk. The gauze had a mesh 0.06 centim. square, with wire 0.02 centim. thick. It was found necessary to use a wider mesh for the lower electrode to allow the flame to pass easily. The grating on the lower disk was, therefore, made by winding platinum wire between

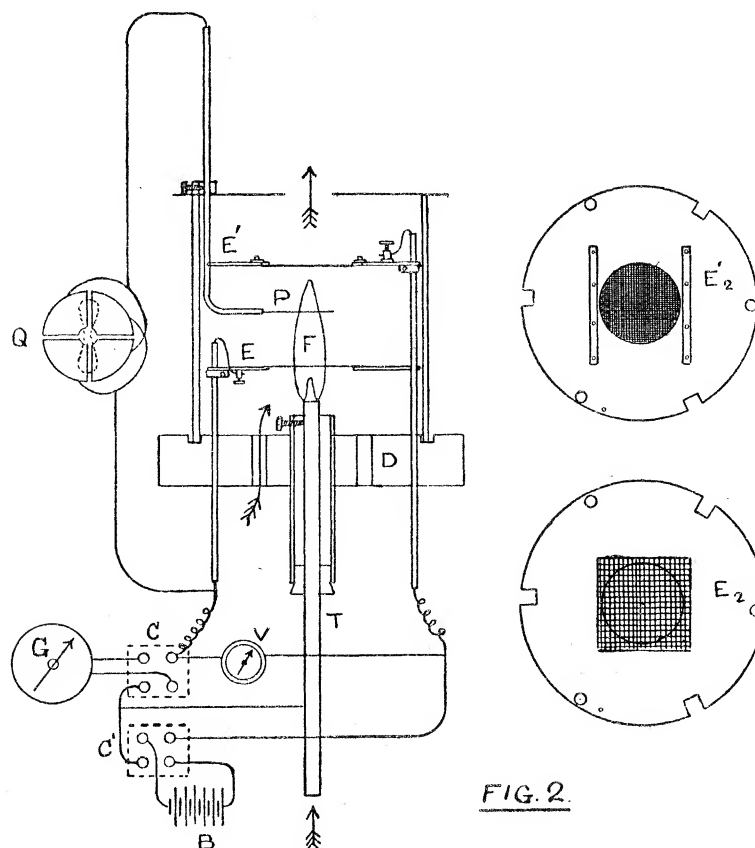


FIG. 2.

- |       |                                   |       |                        |
|-------|-----------------------------------|-------|------------------------|
| F,    | Flame.                            | Q,    | Quadrant electrometer. |
| D,    | Wood block.                       | C C', | Commutators.           |
| T,    | Flame tube.                       | G,    | Galvanometer.          |
| E E', | Electrodes.                       | V,    | Voltmeter.             |
| E'2,  | Upper surface of upper electrode. | B,    | Battery.               |
| E2,   | Upper surface of lower electrode. |       |                        |

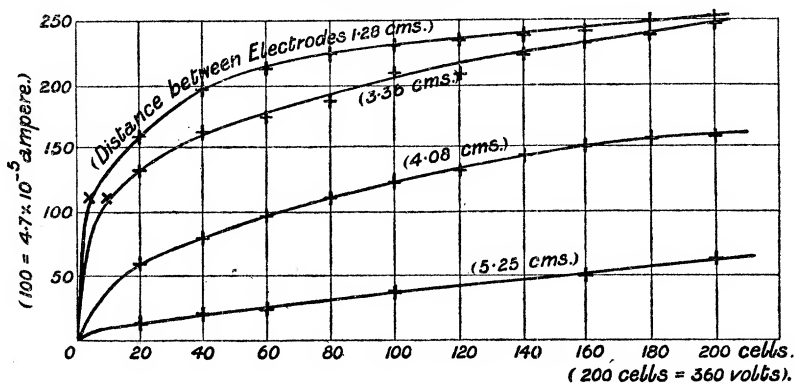
small brass pegs fixed in the upper surface of the disk. The wires were 0.3 centim. apart.

The lower electrode was connected through a galvanometer to one pole of a battery of small secondary cells, and the upper electrode was connected to the other pole. The flame tube was also connected to the same pole of the battery as the lower electrode. The potential difference between the two electrodes could be measured by means of a multicellular electrostatic voltmeter when it was above 250 volts. A

circular patch at the centre of the grating on each electrode was heated by the flame. The lower electrode was nearly white hot usually, and the upper red hot, more or less, according to its position.

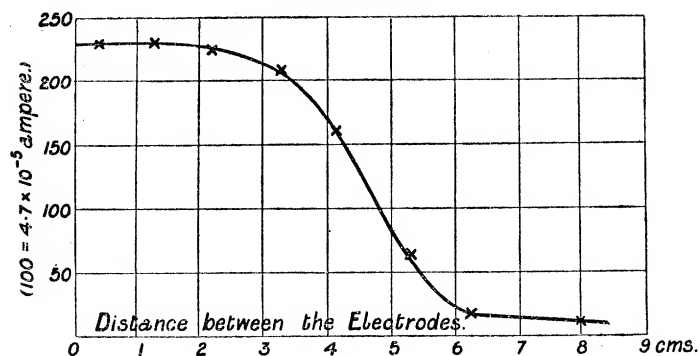
Diagram No. 1 shows the relation between the current and E.M.F. when a  $\frac{1}{20}$  normal solution of potassium carbonate was sprayed for four positions of the upper electrode, which was charged positively, the lower electrode being in the same position in each case, viz., 5.6 centims. above the flame tube.

Diagram No. 1.



It will be observed that as the distance between the electrodes is increased, the E.M.F. necessary to produce approximate saturation increases very rapidly, but the saturation value of the current, where it is actually reached, is independent of the position of the upper or positive electrode. Diagram No. 2 shows the relation between the current with 200 cells and the distance between the electrodes, the lower electrode being kept fixed and negatively charged as before.

Diagram No. 2.



The falling off in the current as the upper electrode is raised is very rapid at from 3 to 6 centims. distance. Up to 3 centims. distance the temperature of the upper electrode remained sensibly constant, but above this distance it became cooler as the electrode was raised higher in the flame, and at 6 centims. distance it was only red

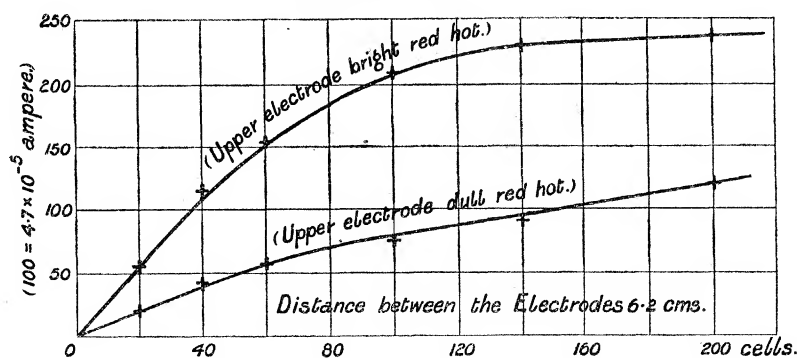
at the centre, but it remained visibly hot even at 9 or 10 centims. above the lower electrode. It appeared probable that the cooling of the upper electrode might affect the observed current, and to test this point an electrode was constructed similar to those already described, but so arranged that the grating of platinum wires could be heated by passing an electric current through it. The grating was insulated by strips of mica, and the battery used to heat up the grating was insulated, and one end of the grating wire connected to the brass disk supporting it.

It was found that when the upper electrode was kept at a bright red heat in this way the current, with 200 cells, was independent of the position of the upper electrode up to 8 centims. above the lower electrode. The following table gives some of the numbers obtained with 200 cells.

Distance between the Electrodes.	Current.	
	Upper Electrode not heated.	Upper Electrode heated.
centims.		
1.3	235	235
3.0	236	234
4.2	180	230
6.2	18	227
8.0	10	235

Diagram No. 3 shows the change in the relation of the current to the E.M.F. when the upper electrode is heated in this way.

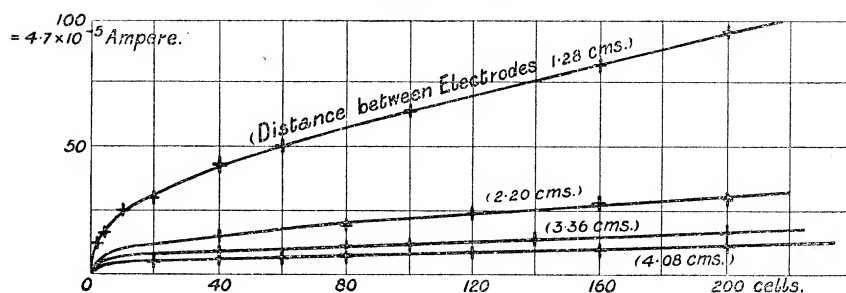
Diagram No. 3.



Thus it appears that keeping the upper electrode hot enables the current to attain its saturation value with a much smaller E.M.F. than is necessary when the electrode is not specially heated.

Diagram No. 4 shows the relation between the current and E.M.F. for several positions of the upper electrode when this is negatively charged, the lower electrode being in the same position in each case as before.

Diagram No. 4.

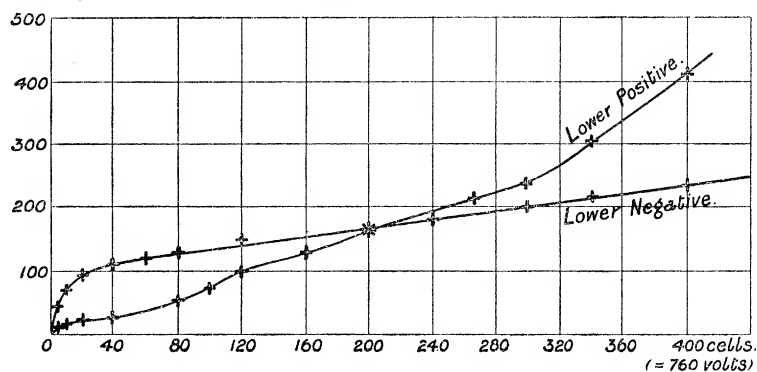


In this case, in which the positive or lower electrode is hotter than the negative electrode, the current does not show much sign of arriving at a saturation value as the E.M.F. is increased. To see whether this depends on the relative positions of the electrodes with reference to the direction of motion of the flame gases, the lower electrode was fixed very near the base of the flame, so that it was less heated than the upper electrode. It was then found that when the lower electrode was positive, the current became nearly saturated with about 100 cells, whereas when the lower electrode was negative, the current showed no sign of attaining a saturation value.

Thus the saturation of the current depends on the temperatures of the electrodes, and not on the motion of the flame gases.

Diagram No. 5 shows the relation between the current and E.M.F. when the distance between the electrodes was 0.3 centim., the lower electrode being slightly hotter than the upper electrode.

Diagram No. 5.

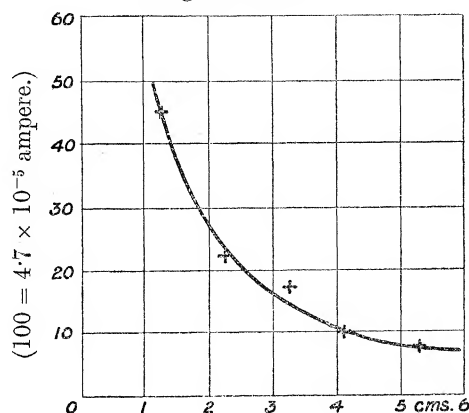


When the E.M.F. is less than 150 volts the two curves are similar to those obtained when the electrodes were at greater distances apart, but at higher E.M.F.'s the current with the lower electrode positive increases rapidly with the E.M.F., and becomes greater than that with the lower electrode negative. In all these experiments except those in which the upper electrode was heated by an electric current, the heated surface on the upper electrode was considerably greater than that on the lower electrode, owing to the upper electrode being of finer gauze than the lower electrode, but the lower electrode was usually heated to a higher temperature than

the upper electrode, partly because, owing to its wider mesh, it lost heat less readily by conduction to the brass disk supporting it.

Diagram No. 6 shows the relation between the current and the distance between the electrodes when the lower electrode is positive and kept fixed for an E.M.F. of 70 volts per centim. of distance between the electrodes.

Diagram No. 6.



The current was always greater when the hotter electrode was negative than when it was positive, except when the electrodes were very near together, so that a very great electromotive intensity could be applied.

The following table gives some of the currents observed showing this:—

E.M.F.	Height of Lower Electrode above the Flame tube.	Distance between the Electrodes.	Current. (100 = $4.7 \times 10^{-5}$ ampere.)	
			(1) Lower +	(2) Lower -
volts.	centims.	centims.		
335	5.6	1.28	75	233
100.5	5.6	1.28	36.5	198
330	5.6	2.20	30	233
370	5.6	6.2	10	18
725	5.6	0.3	407	235
350	3.65	3.35	16	355
175	3.65	3.35	10.5	315

The theoretical bearing of the results described in this section of the paper is discussed in Section 7.

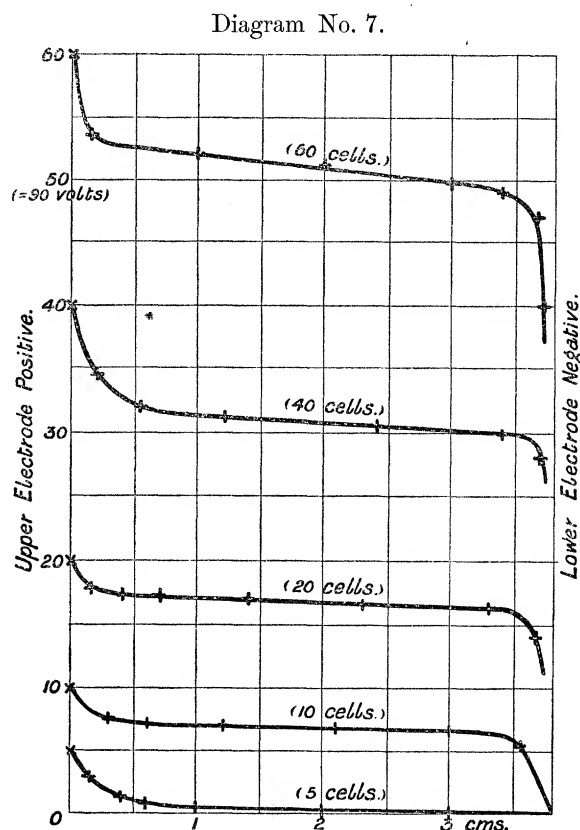
### (3.) *The Fall of Potential between the Electrodes.*

To examine the fall of potential along the flame between the electrodes, a horizontal insulated platinum wire was put in the flame, and its potential measured either by means of a quadrant electrometer or by connecting it through a galvanometer to a

point on the battery used to charge the electrodes and adjusting the position of the wire until no current passed through the galvanometer. The wire and connections with the electrometer are shown in fig. 2.

The wire took up the potential of the flame very quickly, so that even if it was connected to earth through a high resistance its potential was not affected appreciably. The wire was always kept as nearly as possible so as to pass through the axis of the flame; if this was not done the potential curves obtained were considerably altered, although their general character remained the same.

Diagram No. 7 shows some of the results obtained when the electrodes were 3·8 centims. apart, the upper electrode being positively charged and the salt solution sprayed a  $\frac{1}{50}$  normal rubidium chloride solution.



In this case, in which both of the electrodes were bright red hot, the fall of potential between the electrodes is very similar to that observed in gases at low pressures. Near each electrode there is a rapid fall of potential and in the intervening space an approximately uniform small potential gradient. This potential gradient is approximately proportional to the potential difference between the electrodes. The variation of the drop of potential at the negative electrode with the potential difference between the electrodes can be represented by the formula

$$0.873E - 4.4,$$

$$3 \text{ T } 2$$

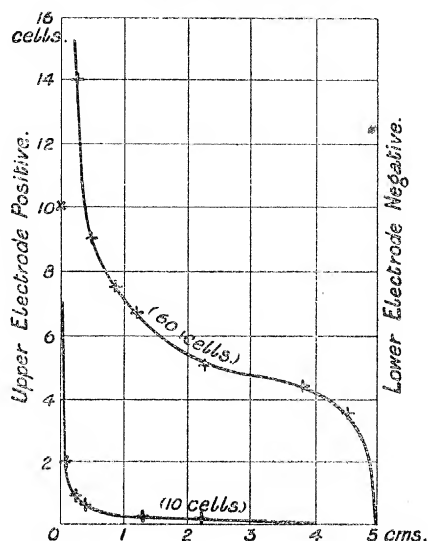
where  $E$  is the P.D. between the electrodes expressed in terms of the E.M.F. per cell used (1.80 volts). When  $E$  is less than about 5 the drop at the negative electrode is zero.

The following table shows this:—

$E$ .	$0.873E - 4.4$ .	Negative drop observed.
60	48.0	48.5
40	30.5	30.0
20	13.1	16.0
10	4.3	6.0
5	0.0	0.0

Diagram No. 8 shows two curves obtained with the electrodes 5 centims. apart, the lower electrode being still in the same position as before.

Diagram No. 8.



In this case the drop of potential at the lower negative electrode did not become appreciable until about 60 cells were used. Moving up the upper electrode to the colder parts of the flame rapidly increased the P.D. at which the negative drop appeared. Thus at 8.8 centims. above the lower electrode there was no negative drop even when 400 cells were used.

When the upper electrode was charged negatively the character of the potential curves was completely changed. In this case nearly all the fall of potential occurred near to the upper negative electrode. Diagram No. 9 shows two curves got with the electrodes 5 centims. apart. Diagrams 10 and 11 each show two curves, one with the upper electrode positively and the other with it negatively charged.

Diagram No. 9.

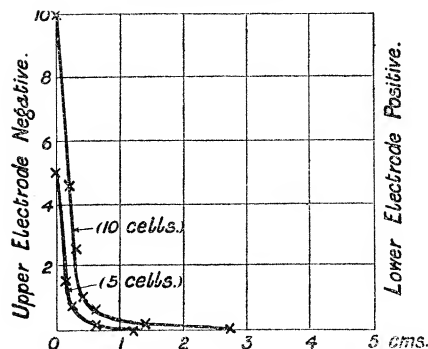


Diagram No. 10.

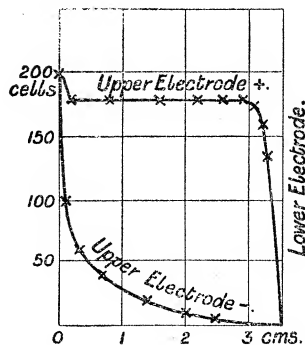
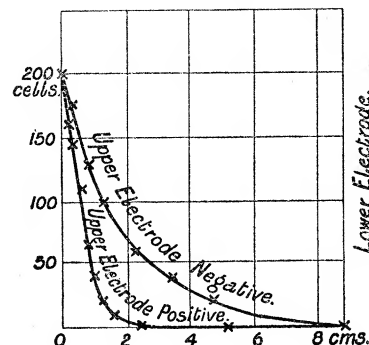


Diagram No. 11.



#### (4.) *The Ionisation of the Salt Vapour.*

ARRHENIUS ('Wied. Ann.,' 42, p. 18, 1891) concluded from the results of his experiments that the conductivity of salt vapours in flames is due to partial ionisation of the salt by the high temperature of the flame, and that the conductivity of a flame containing a salt vapour is very analogous to the conductivity of an aqueous solution of the salt. In our paper referred to above we have not seen any reason to doubt the general accuracy of ARRHENIUS' conclusions.

There are, however, a number of important facts which do not readily lend themselves to explanation by the hypothesis just mentioned. The phenomena of unipolar conduction are among these. HITTOFF (see WIEDEMANN'S 'Elektricität,' vol. 4 B) showed that the current depends very greatly on the negative electrode, and that it is greater when a bead of salt in the flame is near the negative electrode than when it is near the positive electrode, and he concluded that nearly all the resistance to the passage of the current is at or near to the surface of the negative electrode, at any rate in the case of flames free from salt vapour.

The experiments of ARRHENIUS and those described in our paper referred to above, in which the current between two electrodes very near together in the flame was measured, were not adapted for the examination of unipolar conduction and allied phenomena, and it was sufficient, in considering the results obtained, to suppose the conductivity due to ionisation of the salt vapour, without making any further hypothesis as to exactly how and where the ionisation occurs. At the same time, it was more or less tacitly assumed that the salt vapour is ionised throughout the volume of the flame, just as a salt is ionised in an aqueous solution.

I have concluded, from the results described in this paper, that the ionisation of the salt takes place entirely, or very nearly so, at the surface of the glowing platinum electrodes, and not throughout the volume of the flame. The experiments described above on the variation of the current with the distance between the electrodes, show that when the two electrodes are both kept hot, then the saturation current is independent of the distance between the electrodes, whereas if the salt vapour were

ionised throughout the flame, the current should have increased with the distance between the electrodes. To test this more completely, two electrodes of platinum foil, each 1.5 centim. square, were supported opposite one another in the flame so that the distance between them could be easily varied. The salt solution sprayed was a  $\frac{1}{50}$  normal rubidium chloride solution. With this arrangement it was found that, with a potential difference of 800 volts between the electrodes, moving the positive electrode did not affect the current between the electrodes unless it was moved so near to the side of the flame that it became comparatively cool, in which case the current was diminished. Moving the negative electrode usually affected the current, the current being greater the hotter the electrode appeared. If the negative electrode was placed at about the axis of the flame, then it could be moved several millimetres either way without appreciably affecting the current, but the effect of moving it to at all near the sides of the flame was to diminish the current, this effect being much more marked than in the case of the positive electrode.

The amount of salt vapour passing between the electrodes is roughly proportional to the distance between them, so that since the potential difference used was fully enough to approximately saturate the gas, the current should have increased with the distance between the electrodes if the ionisation took place throughout the volume of the flame.

If the two platinum electrodes just described were placed one on each side of the flame, just far enough from it not to be visibly heated, and about half-way up the flame, only a very small current could be passed between them, even when an E.M.F. of 400 volts was applied. This current, moreover, was only slightly increased when the flame was filled with a salt vapour. The following are the currents observed in one case with 45 volts E.M.F. :—

- (1.) Both electrodes just outside the flame and not visibly hot. Distance between the electrodes 2.5 centims.—

Current without salt . . . . .	3 divisions.
Current with $\frac{1}{50}$ $\text{Rb}_2\text{CO}_3$ . . . . .	12 „

- (2.) Both electrodes just inside the flame and red hot. Distance between the electrodes 2 centims.—

Current without salt . . . . .	18 divisions.
Current with $\frac{1}{50}$ $\text{Rb}_2\text{CO}_3$ . . . . .	610 „

It is clear that the heating of the electrodes enormously increases the available conductivity, exactly as though the ionisation did not take place unless the electrodes were red hot. There is, nevertheless, a very small amount of conductivity even when cold electrodes are used, as has been known for a long time. This is no doubt due to a small amount of ionisation really taking place throughout the volume of the flame, both in the case of the flame gases and of the salt vapour.

This conductivity is, however, only a minute fraction of that which is observed when the electrodes are both hot enough to glow. If one electrode only is hot, then the current is much greater than when both are cold, but is still small compared with that obtained when both are hot. The explanation of this is considered in Section 7.

If a piece of platinum foil is put in the flame midway between the two electrodes when both are just outside the flame and not visibly hot, then the current is greatly increased, showing that the presence of the glowing platinum enables ionisation to take place. The following currents were observed with an E.M.F. of 45 volts and  $\frac{1}{50}$  Rb<sub>2</sub>CO<sub>3</sub> :—

- (1.) Both electrodes not visibly hot. Current 12 divisions.
- (2.) With a piece of platinum foil in the flame between the electrodes and insulated. Current 40 divisions.
- (3.) Foil connected to earth. Current 400 divisions.

The great increase in the current on connecting the foil to earth appears to be due to the much greater ease with which an electrode in the flame loses negative electrification than positive. This causes the foil when insulated to be positively charged to nearly the same potential as the positive electrode, which diminishes the current. The explanation of this will be considered in Section 7.

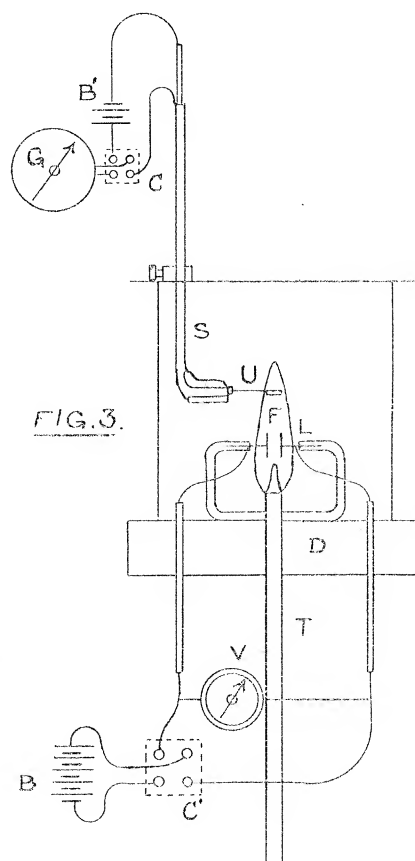
The effect of putting a small bead of salt near the electrodes was also tried, the flame being otherwise free from salt. It was found that if the salt vapour only came in contact with the positive electrode, then the increase in the current due to the salt was very small, whereas if the salt vapour came in contact with the negative electrode the current was greatly increased. If the salt vapour passed between the electrodes without coming in contact with either, then the current was not increased at all. The following numbers were obtained with a bead of potassium carbonate :—

- (1.) Flame without salt. Current 20 divisions.
- (2.) Salt vapour on positive electrode. Current 60 divisions.
- (3.) Salt vapour on negative electrode. Current 720 divisions.

It is clear from this that unless the salt vapour actually comes into contact with the glowing electrodes, the conductivity of the flame is not affected by its presence.

GIESE ('Wied. Ann.,' vol. 17, p. 517, 1882) showed that when two pairs of electrodes were placed one above the other in a flame free from salt, or rather in the gases immediately above the flame, then applying an E.M.F. to the lower pair diminishes the conductivity between the upper pair. This effect was evidently due to the removal of the ions from the stream of gas by the lower pair of electrodes, and should, therefore, not happen in the case of the conductivity of the salt vapour if there is no ionisation of the vapour throughout the volume of the flame. Two pairs of electrodes were arranged as shown in fig. 3. The upper pair was supported by a glass tube passing through the tin plate above the flame, and could be fixed at

any height above the lower pair. The battery and galvanometer connected with the upper pair were insulated so that the electrodes took up the potential of the flame. It was found that applying an E.M.F. to the lower electrodes affected the current between the upper pair very little, if at all, in the case of the conductivity due



U, Upper electrodes.

L, Lower electrodes.

S, Tube supporting upper electrodes.

to a salt vapour. With a  $\frac{1}{20}$  normal solution of potassium carbonate the following currents were obtained; the upper electrodes being about 3 centims. above the lower :—

(1.) No E.M.F. on the lower pair—

Current between the upper pair . . . . 66 divisions.

(2.) 360 volts on the lower pair—

Current between the upper pair . . . . 65 „

With 700 volts on the lower pair the current between the upper pair was slightly increased or diminished, according to the direction of the current between the lower pair, showing that the upper pair took up some of the current from the lower electrodes.

This effect became less as the distance between the two pairs was increased.

The results of this experiment are therefore entirely in accord with the view that the ionisation of the salt vapour takes place only at the surface of the glowing electrodes.

Another experiment very strikingly in favour of this view was also tried. The two horizontal electrodes of platinum gauze were fixed in position about 4 centims. apart in the flame. A bead of potassium carbonate or other salt was then held in the flame between the two electrodes so that the salt vapour only came in contact with the upper electrode. It was found that the current was almost independent of the height of the bead above the lower electrode, unless it was brought so near to the lower electrode that the salt vapour from the bead came into contact with the glowing platinum, when an increase in the current between the electrodes occurred, which was very great if the lower electrode was negatively charged.

The following currents were obtained with a bead of lithium carbonate and potential difference of 380 volts:—

(1.) Bead very near the lower electrode—

Current with lower electrode negative	. .	130.0 divisions.
“ “ “ positive.	. .	4.3 “

(2.) Bead 0.2 centim. above lower electrode—

Current with lower electrode negative	. .	84.0 divisions.
“ “ “ positive.	. .	2.8 “

(3.) Bead 1 centim. above lower electrode—

Current with lower electrode negative	. .	3.5 divisions.
“ “ “ positive.	. .	2.6 “

To further test the view that the salt vapour is not ionised in the flame, except at the surface of the glowing electrodes, the conductivity of the flame alone for very rapidly-alternating currents was compared with that of the flame containing salt vapour by the method described by Professor J. J. THOMSON ('Cambridge Phil. Soc. Proc.' vol. 8, Part V.).

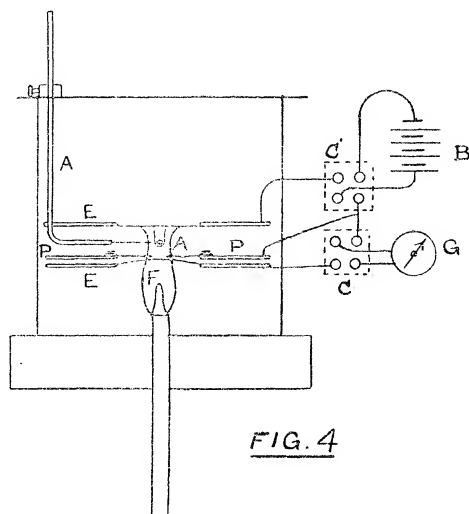
The outer coatings of two Leyden jars were connected through two coils of wire, each consisting of five or six turns of well-insulated wire, and the inner coatings were charged by means of a Whimshurst machine; so that when the charges on the inner coatings were allowed to discharge to each other rapid electrical oscillations passed through the two coils. An electrodeless discharge bulb containing bromine vapour placed in one of the coils served to indicate, by the intensity of the light from its discharge, the absorption of energy when a conductor was placed in the other coil. With this arrangement the conductivity of a large Bunsen flame could be distinctly detected, but the introduction of salt into the flame produced little or no effect, although enough salt was introduced to have increased the current between two electrodes in the flame by several hundred times.

It thus appears that nearly all the ionisation of the salt vapour, to which the conductivity of the flame is due, takes place at the surfaces of the glowing electrodes, although the electrodes are certainly colder than the flame gases. If we regard a molecule of the salt as consisting of oppositely-charged ions or electrons held together by the attractions between their charges, then, when the molecule is very near to a conductor like the electrode in the flame, the induced charges on the conductor diminish the attraction between the ions composing the molecule which may enable it to be ionised, even while the molecules not near the electrodes are quite stable, though at a higher temperature.

(5.) *The Relative Velocities of the Ions in the Flame.*

The way in which the current through the flame depends on the temperature of the negative electrode indicates that the part played by the negative ions in carrying the current is more important than that played by the positive ions. This fact, and the results obtained in investigating the fall of potential between the electrodes, suggested the idea that the velocity of the negative ions, due to a given potential gradient, is much larger than the corresponding velocity of the positive ions.

To test this, experiments were made in which the potential difference between the upper and lower electrodes necessary to cause the positive or negative ions to move down the flame against the upward stream of gases was determined. The apparatus used for this purpose is shown in fig. 4.



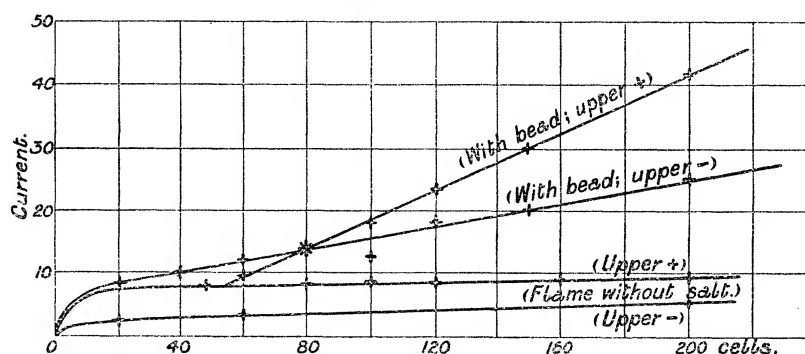
AA, bead of salt and support. P, screen above lower electrode.

A bead of salt was put in the flame between the electrodes, and the current from the lower electrode measured. It was found that when the upper electrode was positive, introducing the bead caused no increase in the current unless the potential difference between the electrodes was greater than 100 volts, when the electrodes

were 5 centims. apart. When the upper electrode was negative, other conditions being the same, the current increased on introducing the bead, even with a potential difference of 1 or 2 volts.

To prevent any ions reaching the lower electrode by passing down the sides of the flame where the velocity of the blast is small, a screen, PP (fig. 4), was placed above the lower electrode. The hole in the platinum gauze of the screen at D was 2 centims. in diameter, and it was completely filled by the flame, which also passed through the gauze round the hole. The platinum grating on the lower electrode was bent up so that it was only 2 or 3 millims. below the gauze screen. Diagram No. 12 shows the results obtained with a bead of potassium carbonate.

Diagram No. 12.



It will be observed that the introduction of the bead produced no increase in the current when the upper electrode was positive until a definite E.M.F. was applied. It was possible to determine this E.M.F. within about 5 volts with certainty with salts of Cs, Rb, and K. With salts of sodium and lithium the amount of current obtained was small compared with the current through the flame without salt, which made it impossible to determine the necessary E.M.F. with any approach to accuracy. The following table gives the results obtained with carbonates of the alkali metals for the positive ions :—

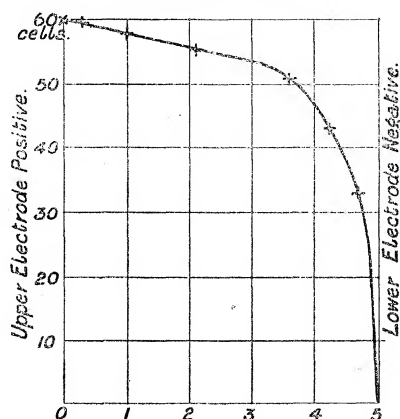
Cæsium. . . . .	104 volts.
Rubidium . . . . .	100 „
Potassium . . . . .	107 „
Sodium . . . . .	90 to 110 „
Lithium . . . . .	90 to 100 „

The E.M.F. between the electrodes 5 centims. apart required to cause the positive ions of the carbonates of K, Rb, Cs, Na, and Li to move down against the blast of the flame is about 100 volts, so that the positive ions of these salts must all have nearly the same velocity due to the slope of potential in the flame. With beads of the

chlorides of the same metals the same result appeared to hold, but the much greater volatility of the chlorides made it difficult to obtain satisfactory results.

To compare the velocity of the positive ion due to a potential gradient of 1 volt per centim. with the velocity of the flame gases, it is necessary to know the potential gradient between the electrodes when the P.D. is just enough to make the ions go down the flame. Diagram No. 13 shows the fall of potential in the flame without salt when this is the case with a P.D. of 107 volts between the electrodes 5 centims. apart, the upper electrode being positive.

Diagram No. 13.



The smallest potential gradient on this curve is 3.3 volts per centim., which is, therefore, the gradient necessary to make the positive ions of the alkali metal salts move against the gases of the flame.

The mean velocity of the mixture of gas and air in the tube leading to the flame was approximately 206 centims. per second, as determined from the volumes of gas and air supplied to the apparatus. On entering the flame the gases of course expand very greatly, but the effect of this expansion is probably not great on the upward velocity of the gases, since the flame is free to expand laterally. Taking the velocity of the gases in the flame as 206 centims. per second, the velocity of the positive ions in the flame due to a potential gradient of 1 volt per centim. is therefore

$$\frac{206}{3.3} = 62 \frac{\text{centims.}}{\text{sec.}}$$

In determining the P.D. necessary to make the negative ions move down against the flame gases, a long wire through which a current was passing was used to supply the potential differences required. Diagram No. 14 shows the results obtained with a bead of  $\text{Na}_2\text{CO}_3$ .

When the E.M.F. is less than 1 volt, there is a small current opposed to the applied E.M.F. At about 1 volt the current with the bead suddenly begins to increase rapidly, with the E.M.F. indicating that the negative ions have begun to go down against the blast of the flame.

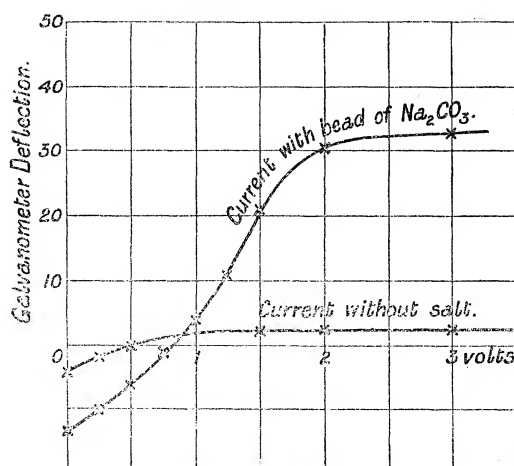
The explanation of the small inverse current when the E.M.F. is small is not easy. It was increased by the introduction of the bead, which may have been due to some salt particles getting carried round to the lower electrode by the circulation of the air between the electrodes. The presence of this inverse current prevented the E.M.F. necessary to bring down the negative ions being determined very exactly, as it varied with the size of the bead and with the volatility of the salt used.

The P.D. required by the negative ions was about 1 volt for both oxy and haloid salts of any of the alkali metals. Taking the potential gradient corresponding to this as 0.2 volt per centim. gives for the velocity of the negative ion due to 1 volt per centim.

$$1030 \frac{\text{centims.}}{\text{sec.}},$$

which is 17 times the corresponding velocity of the positive ions.

Diagram No. 14.



Another method of estimating the velocities of the ions was also tried. Two electrodes of platinum foil were fixed opposite each other in the flame, about 1.5 centim. apart, each electrode being 1.5 centim. square. A bead of salt was held just below one of these, so that the salt vapour only came into contact with this electrode which was connected to earth. The other electrode was charged, and any leak from it measured by the galvanometer. It was found that the current was not increased by the presence of the bead of salt unless the E.M.F. used was greater than a definite amount, which was much greater when the electrode was negatively charged than when it was positively charged. This E.M.F. necessary for the current to increase when the salt is introduced is evidently that required to drag the ions from one electrode to the other, across the blast of the flame gases. The salt vapour from the bead rapidly spreads out in the flame, so that unless the charged electrode was placed near the edge of the flame, the vapour came in contact with both elec-

trodes, in which case the current was increased by the presence of the salt even with very small E.M.F.'s.

It is difficult to form any estimate of the velocities from this experiment, because the ions must spread out from the electrode at which they start by mere diffusion, which will make the velocity appear too great. The fall of potential between the electrodes also is not uniform, and cannot be determined conveniently when the electrodes are so near together. Nevertheless, the results obtained were of the same order of magnitude as those obtained by the method described above. When the electrode was positively charged an E.M.F. of 0.25 volt was enough to increase the current when the salt vapour was introduced. This gives for the velocity of the negative ions  $1200 \frac{\text{centims.}}{\text{sec.}}$ . If the positively-charged electrode was placed outside the flame, then the E.M.F. necessary for the current to increase when the salt vapour was introduced at the other electrode was much greater than before. The following numbers show this. The electrodes were kept at the same distance apart, 1.5 centim. in each case.

- |                                                                                                                                    |            |
|------------------------------------------------------------------------------------------------------------------------------------|------------|
| (1.) E.M.F. required when both electrodes were in the flame . . .                                                                  | 0.25 volt. |
| (2.) E.M.F. required when the charged electrode was at the side<br>of the flame, so as to be only just very slightly red hot . . . | 1.2 volt.  |
| (3.) E.M.F. required when the charged electrode was outside the<br>flame . . . . .                                                 | 2.3 volts. |

The explanation of this increase in the necessary E.M.F. can be readily seen by considering the results of the observations on the fall of potential between the two electrodes when one is much colder than the other. In such a case nearly all the fall of potential occurs near the cold electrode, so that the potential gradient available for dragging across the ions at the hot electrode is very greatly diminished.

A third estimate of the velocity of the negative ions was obtained by diverting the current between two electrodes, one above the other, in the flame by means of a pair of charged electrodes placed outside the flame. Two small platinum electrodes were fixed one above the other in the flame, and 3 centims. apart. The two platinum foil electrodes already described were placed one on each side of the flame, and on a level with the lower of the small electrodes. The lower small electrode was put to earth and the upper one charged positively to  $\frac{1}{10}$  of a volt, and the current from it measured. The two large electrodes were then charged positively, when it was found that the current observed was diminished and reversed if they were charged to more than 0.4 volt. Since the observed current was probably mainly carried by negative ions moving upwards with the blast, because the E.M.F. used was not enough to drag down any positive ions, the stoppage of the current on charging the large electrodes must have been due to the negative ions being dragged across from the lower small electrode to the large electrodes. These latter were 2 centims. apart,

so that the potential gradient between them and the lower small electrode was anyhow less than 0.4 volt. per centim. This gives for the velocity of the negative ions, supposing that they travelled from the lower small electrode to the tops of the larger electrodes, which were 0.7 centim. higher up and 1 centim. distant horizontally,

$$\frac{206}{0.4 \times 0.7} = 740 \frac{\text{centims.}}{\text{sec.}}.$$

This result agrees quite as well as can be expected with the other two estimates made of the velocity of the negative ions due to a potential gradient of 1 volt per centim.

To compare the velocities of the negative ions of various salts some measurements were made of the E.M.F. necessary to drag them from an electrode in the flame to one placed opposite to it, but outside the flame. As I have already mentioned, this E.M.F. increases rapidly as the distance of the outside electrode from the flame is increased. By placing it about 0.5 centim. from the edge of the flame the E.M.F. necessary was increased to about 12.5 volts. This necessary E.M.F. was determined for the following salts, KCL, NaCL,  $\text{Li}_2\text{CO}_3$ , KF, KI, KBr,  $\text{K}_2\text{CO}_3$ , and was found in every case to lie between 12 and 13 volts. Thus it appears that the velocity of the negative ions is independent of the nature of the salt from which they are derived in the flame.

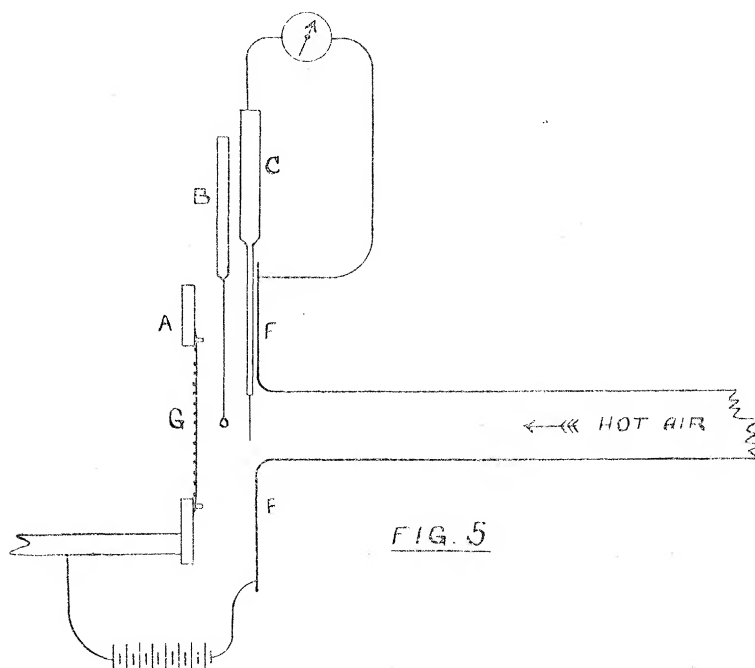
#### (6.) *The Relative Velocities of the Ions in Hot Air.*

The experimental difficulties in the determinations of the velocities of the ions in the flame described above prevented anything more than rough estimations of the respective relative velocities being obtained. I, therefore, endeavoured to devise a method in which the conditions of the experiments should be simpler and more under control. It is clear that the gases of a flame, even when this is kept in as steady a state as possible, are not a very suitable medium for accurate work. I, therefore, tried treating the electrodes by means of electric currents passing through them, and put salt on one or both electrodes. After several trials, with various forms of apparatus, this method was abandoned, owing to the difficulty of getting the air between the electrodes sufficiently hot to keep the salt vapour from condensing.

A new apparatus was now constructed, in which a current of very hot air practically replaced the flame in the experiments already described. The water pump and pressure-regulating apparatus, already described, were used to supply the air. The air was heated by passing it through a platinum tube, 50 centims. long and 1.3 centim. in diameter, maintained at a bright red heat in a Fletcher's gas-tube furnace. The stream of hot air so obtained would heat a platinum wire red hot 5 or 6 centims. from the end of the tube. To prevent the furnace gases getting into the air at the end of the tube, a plane flange of platinum, 6 centims. in diameter, was fitted to the end of the tube.

Fig. 5 shows the essential parts of the apparatus for getting the velocity of the ions in the stream of hot air.

F is the flange on the platinum tube. An electrode, A, consisting of a grating of platinum wires, 0.25 millim. in diameter and 2 millims. apart, wound on pegs in a brass disk, 5.5 centims. in diameter, was placed opposite to the flange, and the stream of hot air kept the grating red hot. This electrode could be charged up by means of battery of small accumulators, and so an electric field maintained between A and F. A small bead of the salt to be investigated was put midway between A and F in the current of hot air, and was supported by a platinum wire held by a glass tube, B.



An electrode, C, was also introduced into the stream of hot air as near the mouth of the tube as possible. This consisted simply of a ring of fine platinum wire supported in a glass tube, which insulated the wire leading to the ring.

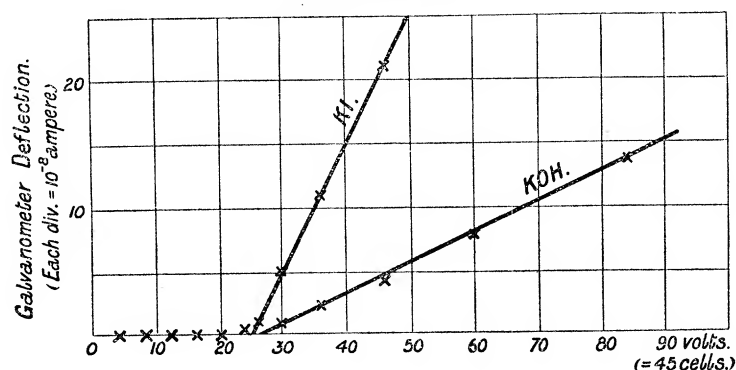
The ring electrode was connected to a galvanometer of 11,000 ohms resistance, and through this to the platinum tube, which was also connected to "earth." The bead of salt was slowly volatilised in the current of hot air and its vapour passed through the grating. On the hot grating some of it was ionised, and if the electric field between the grating and the ring electrode and flange was strong enough, some of the ions moved against the blast of air to the ring electrode, so producing a current which was indicated by the galvanometer.

It was thus possible to determine the P.D. necessary to make the ions move against the blast of hot air exactly in the same way as was done in the flame. If the velocity of the blast and the potential gradient corresponding to this necessary P.D. were known, the absolute velocity of the ions could be at once calculated, but, unfortu-

nately, it is not possible to get anything more than rough estimates of these quantities. All that was attempted, therefore, was to determine the necessary P.D.'s for various ions under the same conditions. This gives the relative values of their velocities in the hot air.

The following diagram shows the variation of the current with the P.D. when the platinum flange and the grating electrode were 1 centim. apart, the grating being positively charged with beads of KI and KOH :—

Diagram No. 15.



It will be observed that in each case the current is zero until a P.D. of about 25 volts. is reached, when it increases nearly uniformly with the P.D.

Other conditions remaining the same, the necessary P.D. should vary directly as the distance between the electrodes. Actually it was found that the necessary P.D. increased more rapidly than the distance, except when this was less than about 1.5 centim. Below 1.5 centim. distance, the necessary P.D. varied as the distance between the electrodes. Thus the following results were obtained with a  $\text{Rb}_2\text{CO}_3$  bead :—

Distance between Electrodes.	Necessary P.D.
centims.	cells
1.5	17.5
1.0	12.5
0.8	9.5

With other salts similar results were obtained. In most of the measurements made the grating and the flange were kept 1 centim. apart.

The effect of varying the velocity of the air blast was also tried. It was found that for small variations of the velocity not greater than 20 per cent. of its usual value, the necessary P.D. varied directly as the velocity of the blast. The blast could not be increased more than about 20 per cent. with the apparatus available. For diminu-

tions of the velocity of the blast greater than 20 per cent., the necessary P.D. diminished more rapidly than the velocity of the blast. This was probably due to the effects of accidental air currents and diffusion, which, of course, become more important when the blast of air is made less rapid. If the velocity of the blast was reduced to much less than one-half its usual value, the grating did not become hot at all, and practically no current at all could be obtained.

Any change in the temperature of the platinum tube produced a change in the amount of current obtained with any given P.D., and also changed the value of the least P.D. necessary to give an appreciable current.

The gas and air supplies to the gas furnace were therefore carefully regulated by means of the apparatus already described for producing a steady flame. In this way the temperature of the tube could be maintained sufficiently constant for any length of time.

Increasing the temperature increased the amount of current obtained, and diminished slightly the least necessary P.D.

Since, however, altering the temperature of the tube alters so many of the other conditions of the experiments, such as the velocity of the air blast and the rate of volatilisation of the salt bead, it is very difficult to interpret the meaning of this last result. Consequently in all the experiments the temperature of the tube was kept as nearly as possible the same.

The accuracy with which the necessary P.D. could be determined varied with the distance between the electrodes and with the temperature of the tube. If the electrodes were too near together, a current was obtained with any P.D., however small.

Increasing the temperature diminished the least distance at which satisfactory results could be obtained.

Finally, a distance of 1 centim. between the electrodes and a definite supply of gas and air to the furnace and to the tube were adopted, as giving the best results. The P.D. necessary to produce an appreciable current could be determined within 1 volt in any one experiment, and the results of different experiments with the same salt usually agreed within the same limit.

Occasionally larger discrepancies than this occurred, which, however, could generally be traced to some accidental circumstance affecting the supply of gas or air to the furnace.

The amount of current obtained with any one salt depended much less than might be expected on the size of the bead used. With some very volatile salts such as KI, a bead about 3 millims. in diameter only lasted two or three minutes, yet during nearly all this time the current with a given P.D. remained very nearly constant and only began to fall off when the bead had almost disappeared. This, of course, greatly facilitated the measurements, since it was not necessary to keep the bead very constant in size during a series of determinations of the current with different P.D.'s.

The rate at which the current increased with the P.D. after the least necessary P.D. was reached varied greatly with different salts, and with the sign of the charge on the grating. In general, the salt which was the more volatile gave the greater rate of increase of current with P.D. The rate of increase of current with P.D. was also usually greater when the grating was negatively charged than when it was positively charged.

When the grating was negatively charged it was found that the P.D. at which the current began to increase with the P.D. between the electrodes was, other conditions remaining unchanged, approximately 7.0 volts for all the salts tried, viz. :—

$\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{NaCl}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ ,  $\text{KF}$ ,  $\text{LiCl}$ ,

$\text{Li}_2\text{CO}_3$ ,  $\text{RbCl}$ ,  $\text{Rb}_2\text{CO}_3$ ,  $\text{CsCl}$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{Ba}(\text{NO}_3)_2$ .

The following salts were also tried, but although they gave a large amount of current, it was so unsteady and lasted such a short time, owing to the decomposition of the salt, that no definite results could be obtained :  $\text{FeCl}_3$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{MgCl}_2$ .

When the grating was positively charged, the least necessary P.D. was very approximately 25 volts with each of the salts of Li, Na, K, Rb, and Cs mentioned above, and very approximately 48 volts for each of the salts of Ca, Sr, and Ba.

The mean velocity of the air blast was estimated to be about  $180 \frac{\text{centims.}}{\text{sec.}}$ , which gives for the velocities of the ions due to one volt per centim. the following values :—

(1.) Negative ions . . . . .	26	$\frac{\text{centims.}}{\text{sec.}}$
(2.) Positive ions of salts of Li, Na, K, Rb, and Cs . . . . .	7.2	$\frac{\text{centims.}}{\text{sec.}}$
(3.) Positive ions of salts of Ba, Sr, and Ca . . . . .	3.8	$\frac{\text{centims.}}{\text{sec.}}$

Only the relative value of these velocities has any pretensions to accuracy. As already explained, it was not found possible to obtain more than the order of magnitude of the absolute velocities.

The result obtained for the velocities of the ions in the flame, viz., that all the negative have the same velocity, and likewise the positive ions of salts of Li, Na, K, Rb, and Cs, was thus found to hold good also in hot air.

The velocities in the hot air are much smaller than those in the flame. The values given for the velocities in the hot air were obtained by assuming the fall of potential between the grating and the ring electrodes to be uniform. Since there was practically no current between them up to the least necessary P.D., this assumption cannot be very far from correct; still, any departure from a uniform fall would cause the values given to be too small.\*

\* Since the salt vapour is not ionised till it reaches the hot gauze, there are no ions between the gauze and flange unless the ions go against the blast.

Taking this source of error into account, it is still clear that the velocities in the flame are very much greater than those in the hot air. The average temperature of the flame may be taken as say  $2000^{\circ}\text{C.}$ , whilst that of the hot air was nearly  $1000^{\circ}\text{C.}$ ; consequently, if the size of an ion is supposed to be independent of the temperature, the velocity of the ions in the flame should have been about double that in the hot air. Actually the negative ions were found to move forty times quicker in the flame than in the hot air.

The results obtained by McCLELLAND\* for the velocities of the ions in the hot gases coming from flames appear to bear on this point. He found that the velocity of the ions rapidly diminished as the distance from the flame was increased, and this pointed to "a rapid condensation on the charged carrier of some uncharged body greatly increasing its mass."

The theoretical velocity of an ion supposed to be one atom, carrying the same charge that an ion does in solutions, can be calculated by means of the formula

$$u = \frac{Xe}{mk} D$$

where  $u$  is the velocity of the ion,

$D$  the coefficient of interdiffusion of the ions and the gas,

$m$  the mass of an ion,

$e$  the charge on it,

$X$  the electromotive intensity,

$k$  the quotient of pressure by density for the ions.†

This gives for the velocity of an ion of molecular weight 32 in air at the ordinary temperature about 40 centims. per second. At a temperature of  $2000^{\circ}\text{C.}$ , its velocity would be 300 centims. per second, and at  $3000^{\circ}\text{C.}$ , about 400 centims. per second.

The velocity of the negative ions in the flame, 1000 centims. per second, is, therefore, of the same order of magnitude as the theoretical velocity of an ion consisting of one atom.

All the other velocities are less than this, which indicates that the ions consist of clusters of atoms, that is, assuming that they carry the same charge as the ions in electrolysis of solutions. This result is in agreement with those of RUTHERFORD on the velocities of the ions in Röntgen ray and uranium ray conductivity, and of McCLELLAND on the velocities of the ions in the hot gases coming from flames.

The size of this cluster appears to be much greater in the case of positively-charged ions than in the case of negatively-charged ions. ZELENY ('Phil. Mag.,' July, 1898) has shown that the velocity of the negative ions produced in gases by

\* 'Phil. Mag.,' July, 1898.

† See J. J. THOMSON, 'Brit. Assoc. Report,' 1894, Art., "Diffusion," 'Encyclopædia Britannica,' and E. RUTHERFORD, 'Phil. Mag.,' Nov., 1897.

Röntgen rays is greater than that of the positive ions in air by about 25 per cent. McCLELLAND has found the same thing for the ions in the gases coming from flames, and RUTHERFORD has shown that the same result holds good for the ions produced by uranium radiation.

In the flame the negative ions of alkali salt vapours move 17 times as fast as the positive ions, and in air at  $1000^{\circ}\text{C}$ . 3.6 times faster with alkali salts, and 7 times faster with salts of Ba, Sr, and Ca.

It seems reasonable to suppose that since the ions in each of the three classes, viz. :

- 1 Negative ions,
- 2 Positive ions of alkali metal salts,
- 3 Positive ions of Ba, Sr and Ca salts,

have equal velocities, they are equal clusters of atoms. It thus appears that ions which in solutions have equal charges, have equal velocities in the gaseous state. This points to the conclusion that the size of the cluster of atoms forming a gaseous ion, depends, at a given temperature, only on the charge on the ion. Those ions, therefore, which have equal charges, have also equal velocities in the same medium.

#### (7.) *Conclusion.*

Since the ionisation on which the conductivity of the salt vapour depends takes place entirely at the surfaces of the glowing electrodes, there is therefore at the surfaces a thin layer in which very rapid ionisation and recombination are going on. The number of ions dragged out from the surface of an electrode will depend on the slope of potential at the surface, and if this is great enough to drag out all the ions of one sort before they can recombine the current will be as great as possible. Owing to the much greater velocity of the negative ions they will be far more easily dragged out than the positive ions, so that unless the slope of potential is great enough to drag out all of either kind of ions, the current from an electrode with a given slope of potential at it will be greater when the electrode is negatively charged than when it is positively charged.

Consider the case in which one electrode is white hot and the other comparatively cool, so that little or no ionisation occurs at it. In this case only one kind of ions will be present in the space between the electrodes, viz., those of the same sign as the hot electrode, so that there will be a charge in the gas which will diminish the slope of potential near the hot electrode and increase it near the cool electrode. The experimentally-determined slopes of potential with one electrode cool show this effect very clearly.

In this case, in which the fall of potential is nearly all at the cold electrode, the smallness of the potential gradient at the hot electrode is not favourable to the attainment of the saturation value of the current, and the current E.M.F. curves

consequently continue to slope up, even with the greatest E.M.F.'s that could be applied.

If the electrodes are connected to the galvanometer simply without any battery, there is a small deflection indicating a current from the colder electrode to the hotter through the flame. This is easily explained by supposing that some of the negative ions at the electrode diffuse out, owing to their high velocity leaving an excess of positive behind. The blast of the flame will assist this action by blowing away the negative ions as soon as they get away from the surface of the electrode. According to this the hotter electrode loses more negative ions than the colder, since there are more ions formed at it. In the same way a wire immersed in the flame becomes positively charged. This action is almost exactly analogous to the charging of a polished zinc plate, when ultra-violet light falls on it, described by HALLWACHS, RIGHI, and others.

If both the electrodes are hot enough to produce ionisation, and if the fall of potential at the upper electrode is great enough to make the ions from it come down against the blast, then there will be both sorts of ions present in the space between the electrodes, which will modify the fall of potential. Since the positive ions move so much more slowly than the negative ions, they remain in the gas much longer and so have a greater effect on the fall of potential; consequently the fall of potential is much greater at the negative electrode than at the positive electrode. The great velocity of the negative ions enables a much smaller slope of potential to drag them all out than is required to drag out the positive ions, so that unless the E.M.F. applied is very great the current is mainly carried by the negative ions. These points are very well illustrated by the experiments described above, on the effect of specially heating the upper electrode when it is positive. When it is heated the positive ions coming from it transfer the fall of potential from the positive electrode to the negative electrode, so that all the negative ions there are dragged out and the current attains its saturation value as far as the negative ions are concerned.

If the positive electrode only is hot then the positive ions moving across will cause all the fall of potential nearly to be at the negative electrode, and owing to their small velocity this effect will be more complete than when the negative ions alone are present. Owing to this, and to the greater difficulty of dragging out the slow positive ions from the electrode, the current, when the positive electrode is hot, will be much smaller than when the negative electrode is hot. In this way it is easy to explain all the phenomena of unipolar conduction.

In the case where both electrodes are hot, the fall of potential being mostly at the negative electrode, the current due to the negative ions attains its saturation value at a comparatively small E.M.F., but the current carried by the positive ions continues to increase nearly uniformly with the E.M.F.

According to this then, in the equations

$$C = I + k_1 E,$$

$$I - i = k_2 \frac{i^2}{E^2},$$

$I$  is the maximum current carried by the negative ions coming from the negative electrode, and  $k_1 E$  is the current due to the positive ions, which is still far from its saturation value.

If  $E$  is made sufficiently great, the current due to the positive ions should also become saturated, and with very high E.M.F.'s it is found that the current increases less rapidly with the E.M.F. than the formula  $C = I + k_1 E$  represents.

The equation  $I - i = k_2 \frac{i^2}{E^2}$  was originally obtained for the conductivity of Röntgenised gases in which most of the ionisation takes place throughout the volume of the gas. In this case  $k_2 = \frac{\alpha l^3}{\epsilon U^2}$ , where  $\alpha$  is the constant in the equation  $\frac{dN}{dt} = \alpha N^2$  representating the rate of recombination of the ions,  $l$  is the distance between the electrodes,  $\epsilon$  the charge carried by each ion, and  $U$  the sum of the velocities of the positive and negative ions under an electromotive intensity of one volt per centim.

When all the ionisation takes place at the surfaces of the electrodes, the above signification of  $k_2$  no longer holds, but the fact that the equation can still represent the observed relation between the current and E.M.F. shows that the general nature of the conductivity is the same in both cases.

In our paper referred to above, we showed that the conductivity of the halogen salts is approximately proportional to the square root of the concentration of the salt vapour in the flame. The conductivity of the oxysalts followed the same law when the concentration was very small, but with greater concentrations was nearly proportional to the concentration of the salt vapour. Now when the concentration of the salt vapour in the flame is very small, the amount of salt in an extremely thin layer at the surface of an electrode in the flame will be proportional to  $C^{\frac{1}{3}}$ , where  $C$  is the concentration of the salt vapour, that is, supposing that the mean distances between the molecules of salt is larger than the thickness of the layer in which ionisation takes place. Consequently the conductivity should vary as  $C^{\frac{1}{3}}$  if it is supposed that the amount of ionisation is proportional to the amount of salt in this layer. If the concentration of the salt vapour in the flame is so great that the mean distance between the molecules of salt is small compared with the thickness of this layer, then the amount of salt in the layer will be proportional to the concentration of the salt in the flame, so that at such concentrations the conductivity should be proportional to the concentration.

In the following table the observed conductivity of KCL is compared with the calculated by assuming it proportional to (1)  $C^{\frac{1}{3}}$ , (2)  $C^{\frac{1}{2}}$  :—

Concentration of solution, sprayed.	Current calculated.		Current observed.*
	(1.)	(2.)	
0.2	(31.9)	(31.9)	31.9
0.1	22.6	20.1	21.0
0.05	15.9	12.7	14.1
0.01	7.14	4.33	6.0

It will be observed that in each case the observed current lies between the two calculated currents.

The results of the observations described above on the fall of potential between the electrodes show that there is a very close analogy between the conductivity of salt vapours in flames and the conductivity of gases at low pressures. In both cases there is a greater fall of potential near the negative electrode than near the positive electrode, with a small slope of potential in the intermediate space, and it seems very likely, therefore, that the peculiar form of the fall of potential in gases at low pressures is due, like that in the flame, to a great difference between the velocities of the positive and negative ions.

In conclusion, I desire to express my best thanks to Professor J. J. THOMSON for many valuable suggestions during the course of these experiments, and also to Professor A. SMITHELLS for his kindness in allowing me to continue the investigation of this subject begun in his laboratory.

\* These numbers are taken from the previous paper on this subject.